

TASK STATUS REPORT

TASK 1.1 - PI, INSTITUTION: Vincent Battaglia, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Analysis - Cell Fabrication and Materials Characterization

SYSTEMS: High-voltage, high-energy: Gr/1 M LiPF₆ in EC:DEC (1:2)/LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂

BARRIERS: High energy system: low energy, poor cycle life

OBJECTIVES: 1) Bring fundamental understanding to electrode and cell construction. 2) Provide a comprehensive, independent assessment of promising materials with regard to meeting high-power or high-energy performance and cycling requirements, and differentiate between material and cell failure.

GENERAL APPROACH: Objective 1) is achieved through engineering design analysis of each of the steps of the electrode fabrication process and determining why certain configurations of binder and conductive additive work better for a given active material. Objective 2) is achieved through the identification and application of key diagnostic techniques that allow for the physical, chemical, thermal, and electrochemical characterization of materials as they relate to battery performance for advanced transportation applications.

STATUS OCT. 1, 2009: Correlations between electrode cyclability and mechanical strength are being developed. A new binder was synthesized for using Si nanoparticles as an anode: electrodes cycled at C/10 have shown a capacity of 2000 mAh/g for 150 cycles with little to no power fade after 40 cycles. A graphite has been selected as the new baseline, replacing MCMB. A new, high-voltage electrolyte showed improved coulombic efficiency when cycled in Li/NCM cells using cut-off voltages from 4.1 to 4.5 V. It was determined that VC has no measurable effect on the coulombic cycling efficiency of a graphite electrode.

EXPECTED STATUS SEP. 30, 2010: Correlation of electrode mechanical properties to cyclability will be established. The source of self discharge will be identified. We will know the extent to which the oxidation of the electrolyte is cathode material dependent. We will know the fundamental advantages and disadvantages of SBR binder.

RELEVANT USABC GOALS: PHEV-40: 144 Wh/l, 4000 deep-discharge cycles.

MILESTONES:

- (a) Report the coulombic efficiency of baseline NCM vs. graphite and vs. a lithium counterelectrode. (Jan. 10) **Complete**
- (b) Report performance characteristics of a SBR-CMC-binder based anode. (Mar. 10) **Complete**
- (c) Distribute electrodes cycled to different cut-off voltages to other members of the BATT program. (Apr. 10) **Complete**
- (d) Report the results of the mechanical properties vs. cycling capability of NCM-PVdF-based cells. (Sep. 10) **Complete**

PROGRESS TOWARD MILESTONES

(a) Report the coulombic efficiency of baseline NCM vs. graphite and vs. a lithium counterelectrode. (Jan. 10) **Complete**. See 2nd Quarter Report.

(b) Report performance characteristics of a SBR-CMC-binder based anode. (Mar. 10) **Complete**. See 1st Quarter Report.

(c) Distribute electrodes cycled to different cut-off voltages to other members of the BATT program. (Apr. 10) **Complete**. See 3rd Quarter Report.

(d) Report the results of the mechanical properties vs. cycling capability of NCM-PVdF-based cells. (Sep. 10) **Complete**. See 4th Quarter Report.

Other work beyond the milestones.

To provide further insight as to why electrodes fail, efforts with several vendors have resulted in the conversion of a coin cell into a three-electrode cell. Part of the process in making this cell required making a new jig for our coin-cell assembly. Early attempts at this provided warnings as to the sensitivity of Li-ion chemistry to water intrusion. The slightest imperfection of the seal led to side reactions that occurred at greater than three times the rate of a well-sealed cell. It is believed that this is the first time a lab has produced a three-electrode cell that can be used for long-term cycling. As evidence to this, three coin cells were built from the same cathode and anode laminates. One of the cells was a typical two-electrode cell of graphite and NCM fabricated using the standard jig that came with the equipment; another cell was also a two-electrode cell assembled with a jig made in the LBNL machine shop; and the third cell consisted of three electrodes assembled using the LBNL jig. The cells were put on C/10 charge/discharge cycles between 3 and 4.3 V. Plotted in Figure 1 is the slippage of the cell capacity with each discharge relative to its previous discharge plotted *versus* cycle number. Since this is a direct measure of the side reaction, and since the side reactions are very sensitive to contaminants, it was considered the most stringent test of our ability to make a well-sealed cell with three electrodes. As the figure shows, the difference in the rate of the side reactions is indistinguishable. (The cells made without a ref. electrode were temporarily taken off test at cycle 15 and then put back on test a week later.)

Following-up on last quarter's report, where it was indicated that the coulombic efficiency of the anode increased when the counter electrode was changed from Li to NCA, investigation of the coulombic efficiency of the cathode revealed no effect upon changing the anode from Li to graphite. This suggests that something about changing from a small to a large voltage difference is responsible for modifying the rate of the side reactions in the cell.

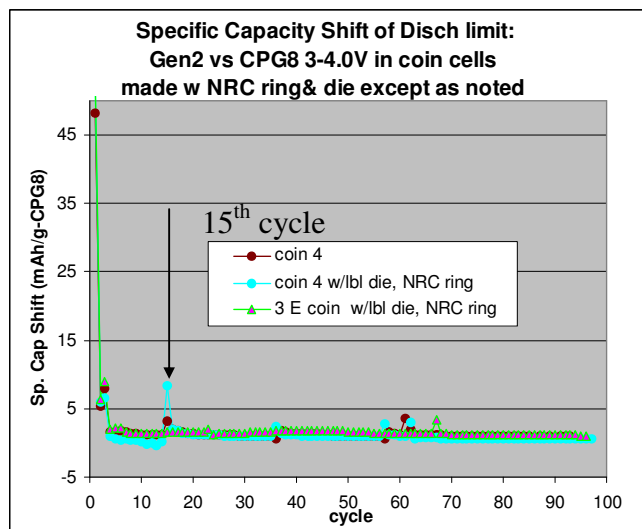


Figure 1. Three separate cells on test. Coin 4 is a cell made with original die and ring, Coin 4 w/lbl die was assembled with an LBL rig, and 3E coin was a three-electrode cell with the LBNL rig.